PRODUCTION OF XYLOSE FROM OIL PALM TRUNK

SITI NAFSIAH BINTI MOHAMED OMAR

A thesis submitted in fulfilment of

the requirementsfor the award of the degree of

Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

PRODUCTION OF XYLOSE FROM OIL PALM TRUNK

ABSTRACT

Oil palm trunk is an oil palm biomass which is the renewable source for the production of many useful products, such as xylose. The study provides efficient analysis on optimizing xylose concentration, in order to obtain higher productivity and yield of xylitol. Xylose is safe, healthy, toxin free substance that can allow people to enjoy the flavor of sugar without negative effects on the body. The objectives of this study are to produce valuable products (xylose and xylitol) from waste oil palm trunk, to identify the effects of sulfuric acid concentration and hydrolysis time on the production of xylose from oil palm trunk. The hydrolysis of oil palm trunk powder was carried out by contacting powder with 3%, 5% and 7% sulfuric acid at 60 °C for 60, 120 and 180 minutes. The acid hydrolysis is using sulfuric acid wood mass ratio of 8: 1 g/g. After hydrolysis reaction, solid part was removed by filtration and the filtrate was neutralized with $CaCO_3$ and then undergoes detoxification process by using activated carbon powdered with the mass ratio 10:1 of hydrolysate/charcoal powder. The percentage of xylose will be analyzed from the hydrolysate by using High Performance Liquid Chromatography machine. From the literature, the results obtained was the higher acid concentrations led to higher sugar recovery but longer hydrolysis's time caused lower amount in sugar recovery. For a conclusion, the high value products which are xylose can be produce from waste oil palm biomass.

PENGHASILAN XYLOSE DARI BATANG KELAPA SAWIT

ABSTRAK

Batang kelapa adalah biomass kelapa sawit merupakan sumber boleh diperbaharui bagi pengeluaran banyak produk yang berguna, seperti xylose. Kajian ini menyediakan analisis yang berkesan dalam mengoptimumkan kepekatan xylose, untuk mendapatkan produktiviti yang lebih tinggi dan hasil Xylitol. Xylose adalah selamat, menyihatkan, bahan bebas toksin yang membenarkan orang ramai untuk menikmati rasa gula tanpa kesan negatif pada badan. Objektif kajian ini adalah untuk menghasilkan produk berharga (xylose dan Xylitol) dari sisa batang kelapa sawit, untuk mengenal pasti kesan-kesan kepekatan asid sulfurik dan masa hidrolisis pada pengeluaran xylose daripada batang kelapa sawit. Hidrolisis serbuk batang kelapa sawit telah dijalankan dengan merendamkan serbuk dengan 3%, 5% dan 7% asid sulfurik pada suhu 60 ° C selama 60, 120 dan 180 minit. Hidrolisis asid menggunakan asid sulfurik kayu nisbah jisim 8: 1 g / g. Selepas tindak balas hidrolisis, sebahagian pepejal telah ditapis dan turasan telah dineutralkan dengan CaCO3dan seterusnya menjalani proses detoksifikasi dengan menggunakan serbuk arang dengan nisbah jisim 10:1 hidrolisat/arang. Peratusan xylose akan dianalisis dari Hidrolisat dengan menggunakan Kromatografi Cecair Prestasi Tinggi mesin. Daripada literatur, keputusan yang diperolehi adalah kepekatan asid yang tinggi membawa kepada penghasilan gula yang lebih tinggi tetapi masa hidrolisis lagi ini disebabkan jumlah yang lebih rendah dalam penghasilan gula. Kesimpulannya, produk bernilai tinggi seperti xylose boleh dihasilkan daripada sisa biomass kelapa sawit.

TABLE OF CONTENTS

	Page
SUPERVISOR'S DECLARATION	ii
STUDENT'S DECLARATION	iii
DEDICATION	iv
ACKNOWLEDGEMENTS	v
ABSTRACT	vi
ABSTRAK	vii
TABLE OF CONTENTS	viii
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF SYMBOLS	xv
LIST OF ABBREVIATIONS	xvi

CHAPTER 1	**INTRODUCTION**	
1.1	Background of Proposed Study	1
1.2	Problem Statement	4
1.3	Objectives	5
1.4	Scope of the research work	5
1.5	Rationale & Significance of Study	6

CHAPTER 2 **LITERATURE REVIEW**

2.1	Oil Palm Biomass	7
2.2	Natural Occurrence of Xylose	9
2.3	Preparation for Samples and Extraction Method for Xylose	11
2.4	Acid Hydrolysis of Xylose	13
2.5	Analytical Methods Analyzing Xylose	15
2.6	Application and Uses of Xylose	16

CHAPTER 3 **METHODOLOGY**

3.1	Introduction	18
3.2	Material	19
3.3	Chemical	19
3.4	Equipment	20
3.5	Experimental Procedure	21
	3.5.1 Materials Preparation of Oil Palm Trunk (OPT)	21
	3.5.2 Acid Hydrolysis of Oil Palm Trunk (OPT)	21
	3.5.3 Charcoal Treatment of Hydrolysate	24
	3.5.4 Analytical Method	25

CHAPTER 4 **RESULT AND DISCUSSION**

4.1	Introduction	26
4.2	pH value every sample before and after	26

	neutralization process with $CaCO_3$	
	4.2.1 Discussion	27
4.3	Composition of oil palm trunk (OPT)	27
	4.3.1 Discussion	28
4.4	Sugar compound detected by HPLC in the oil palm trunk (OPT) hydrolysate	28
	4.4.1 Discussion	29
4.5	Standard xylose concentration based on peak area	29
	4.5.1 Discussion	30
4.6	Xylose concentration recovery for acid hydrolysis of 3% H_2SO_4	31
	4.6.1 Discussion	31
4.7	Xylose concentration recovery for acid hydrolysis of 5% H_2SO_4	32
	4.7.1 Discussion	32
4.8	Xylose concentration recovery for acid hydrolysis of 7% H_2SO_4	33
	4.8.1 Discussion	33
4.9	The xylose recovery after the treatment with acid at different concentrations for different hydrolysis times	34
	4.9.1 Discussion	35
CHAPTER 5	**CONCLUSION AND RECOMMENDATION**	
5.1	Conclusion	36
5.2	Recommendation	37
REFERENCES		40

APPENDICES

Appendix A	Chemstation Data Area and Percent Report of HPLC for sample 1a	40
Appendix B	Chemstation Data Area and Percent Report of HPLC for sample 1b	41
Appendix C	Chemstation Data Area and Percent Report of HPLC for sample 1c	42
Appendix D	Chemstation Data Area and Percent Report of HPLC for sample 2a	43
Appendix E	Chemstation Data Area and Percent Report of HPLC for sample 2b	44
Appendix F	Chemstation Data Area and Percent Report of HPLC for sample 2c	45
Appendix G	Chemstation Data Area and Percent Report of HPLC for sample 3a	46
Appendix H	Chemstation Data Area and Percent Report of HPLC for sample 3b	47
Appendix I	Chemstation Data Area and Percent Report of HPLC for sample 3c	48

LIST OF TABLES

		PAGE
Table 2.1	Proximate analysis of biomass of oil palm biomass (%, dry weight)	9
Table 4.1	pH value for every sample before and after neutralization process with CaCO3	27
Table 4.2	Composition of oil palm trunk (OPT)	27
Table 4.3	Sugar compound detected by HPLC in the oil palm trunk (OPT) hydrolysate	28
Table 4.4	Standard xylose concentration based on peak area	29
Table 4.5	Xylose concentration recovery for acid hydrolysis of 3% H_2SO_4	31
Table 4.6	Xylose concentration recovery for acid hydrolysis of 5% H_2SO_4	32
Table 4.7	Xylose concentration recovery for acid hydrolysis of 7% H_2SO_4	33
Table 4.8	The xylose recovery with the treatment of acid at different concentrations for different hydrolysis times	34

LIST OF FIGURES

		PAGE
Figure 3.1	Analytical Balance	20
Figure 3.2	Orbital shaker	20
Figure 3.3	HPLC	20
Figure 3.4	Oven	20
Figure 3.5	Acid Hydrolysis	22
Figure 3.6	Acid Hydrolysis Filtration	22
Figure 3.7	Acid hydrolysis (sample 1a)	22
Figure 3.8	Acid hydrolysis (sample 1b)	22
Figure 3.9	Acid hydrolysis (sample 1c)	22
Figure 3.10	Acid hydrolysis (sample 2a)	23
Figure 3.11	Acid hydrolysis (sample 2b)	23
Figure 3.12	Acid hydrolysis (sample 2c)	23
Figure 3.13	Acid hydrolysis (sample 3a)	23
Figure 3.14	Acid hydrolysis (sample 3b)	23
Figure 3.15	Acid hydrolysis (sample 3c)	23
Figure 3.16	Neutralisation (Sample 1a)	23
Figure 3.17	Neutralisation (Sample 1b)	23
Figure 3.18	Neutralisation (Sample 1c)	23
Figure 3.19	Neutralisation (Sample 2a)	23
Figure 3.20	Neutralisation (Sample 2b)	23
Figure 3.21	Neutralisation (Sample 2c)	24
Figure 3.22	Neutralisation (Sample 3a)	24
Figure 3.23	Neutralisation (Sample 3b)	24
Figure 3.24	Neutralisation (Sample 3c)	24
Figure 3.25	Charcoal Treatment	24
Figure 3.26	Charcoal Treatment Filtration	24

Figure 3.27	Automatic HPLC	25
Figure 3.28	Acetonitrile (Mobile Phase)	25
Figure 4.1	Composition of oil palm trunk (OPT)	27
Figure 4.2	Sugar compound detected by HPLC in the oil palm trunk (OPT) hydrolysate	28
Figure 4.3	standard curve for xylose concentration	30
Figure 4.4	Xylose recovery for 3% H_2SO_4 hydrolysis	31
Figure 4.5	Xylose recovery for 5% H_2SO_4 hydrolysis	32
Figure 4.6	Xylose recovery for 7% H_2SO_4 hydrolysis	33
Figure 4.7	The xylose recovery after the treatment with acid at different concentrations for different hydrolysis times	34

LIST OF SYMBOLS

%	Percent
g	Gramme
g^{-1}	Recipcrocal gramme
°C	Degree celcius
ml	milliliter
nm	nanometer

LIST OF ABBREVIATIONS

HPLC	High Performance Liquid Chromatography
FTIR	Fourier Transform Infrared Spectroscopy
OPT	Oil Palm Trunk
EFB	Empty Fruit Bunch
OPF	Oil Palm Frond
Wt	Weight
IR	Infrared
UV	Ultraviolet
pH	Potential hydrogen
RPM	Rotation per minutes

CHAPTER 1

INTRODUCTION

1.1 Background of Proposed Study

Malaysia produced an estimated 80 million tonnes/year dry weight of oil palm biomass, reflecting the importance and significant potential of biomass. This biomass includes empty fruit bunches, mesocarp fibres, oil palm shells, oil palm fronds and oil palm trunks. Much of the 70 million tonnes/year of oil palm trunk in 4.7million acre plantation produced is burnt or left to rot. Usually the trunks generated from replanting which causes some environment problems. There are reports on application of the oil palm trunk especially for veneer and plywood production being reported (Hamid *et al.,* 2008). The content of α-cellulose in this waste of oil palm trunk is slightly lower (41%) than wood (45–50%). However, it can play an important complementary role given the possibility of obtaining cellulosic pulp with an α-cellulose content, and therefore has possible applications in producing paper or pasteboard with different characteristics, especially in areas with limited forest resources. Some attempts to characterize the palm trunk fibre as a raw material for paper making have been reported. Khoo et al.,reported that oil palm trunk fibre gave sulphate pulp with moderate yield and strength. The unbleached pulps would be suitable for medium grade wrapping paper.

A part from that, controlled hydrolysis of cellulose and hemicellulose from oil palm wood allows producing several useful chemical products such as xylose furfural, glucose and starch enhancing its economic feasibility (Chin *et al.,* 2010). This study actually is to produce xylose and xylitol from oil palm trunk. Xylose is the main building block for hemicellulose, which comprises about 30% of plant matter. Xylose is otherwise pervasive, being found in the embryos of most edible plants. It was first isolated from wood by Koch in 1881.

Bioconversion of lignicellulose to ethanol or xylitol requires the hydrolysis of carbohydrate polymers to their corresponding monomeric sugars prior to fermentation. Lignocellulose hydrolysis has been achieved either by acid hydrolysis or enzymatic hydrolysis. However, acid hydrolysis is the most commonly applied and the method can be used either as a pretreatment preceding the enzymatic hydrolysis or as a method of hydrolyzing lignocellulose for the sugars. As a consequence, the amount of sugars recovered from the raw material is dependent on the reaction time, temperature and acid concentration. However, acid concentration is the most important parameter affecting sugar yield. Apart from that, the sugar obtained from hemicellulose, other by-products, such as furfural, are also produced during the hydrolysis process.

Xylose is a great alternative to white sugar and has none of the negative side effects of sugar. Xylose is a natural sugar that is found in some woody materials besides palm oil biomass like empty fruit bunch and oil palm trunk it also found in straw, pecan shells, cottonseed hulls and corncobs. It is extracted through a scientific process. Xylose is not metabolized by humans. It is completely absorbed and secreted from the kidneys. In animal medicine, xylose is used to test for malabsorption by administration in water to the patient after fasting. If xylose is detected in blood and/or urine within the next few hours, it has been absorbed by the intestines. Reduction of xylose by catalytic hydrogenation produces the non-cariogenic sugar substitute xylitol.

1.2 Problem Statement

Replanting will cause environmental problems. After approximately 25 years of its economic life span, oil palm trunks are cut down so as to allow replanting, the trunks simply being left on the plantation and not been used productively. During replanting, a very large amount of waste trunks are exhausted and cut into pieces and burned simply to prevent the breeding of harmful insects but will cause local environmental pollution.

On the other hand, the demand and attraction for alternatively material from renewable resource had incredibly increased tremendously. Basically, the oil palm trunks contain lignin, holocellulose and quite significant amount of starch. This research is going to solve the problem of getting the best process for the production of cellulose, hemicelluloses and lignin from oil palm trunk. The production of xylose from oil palm trunk is an alternative to white sugar and as sugar-free sweetener. The high value economic conversion of oil palm wood to chemical products is the production of sugars-free sweetener.

1.3 Objectives

The purposes of this research are:

i. To produce a valuable products (xylose) from waste oil palm trunk
ii. To study the effect of sulfuric acid (H_2SO_4) concentration of the acid hydrolysis process.
iii. To study the hydrolysis time on the production of xylose from oil palm trunk (OPT).

1.4 Scopes of Research Work

i. The reaction hydrolysis time is selected at 60 to 180 min.
ii. The concentration of sulfuric acid (H_2SO_4) is used in range 3 to 7%.
iii. Acid hydrolysis temperature is constant at 60°C.
iv. The percentage of hemicellulose and cellulose need to be measured in the oil palm trunk.
v. The percentage of xylose compound need to be detected in hemicellulose fraction.
vi. The raw material used is oil palm trunk (OPT) powder.
vii. The chemicals used are sulfuric acid (H_2SO_4), calcium carbonate ($CaCO_3$), activated charcoal and acetonitrile HPLC grade.
viii. The equipments used are oven, orbital shaker, high performance liquid chromatography (HPLC) and analytical balance.

1.5 Rationale & Significance of study

i. Oil palm trunk seems to be a bio resource which can be entirely converted into valuable chemicals and products. (waste to wealth)

ii. The increasing interest on use of oil palm trunk for bioconversion to chemicals is justifiable as these materials are low cost, renewable and widespread sources of sugar-free sweetener.

iii. Xylose is a safe, healthy, toxin free substance that can allow people to enjoy the flavor of sugar without negative effects on the body.

iv. Xylose causes the growth of positive elements in the intestines. Through this, more absorption of all nutrients can take place. More absorption of nutrients equals a better overall immune system.

CHAPTER 2

LITERATURE REVIEW

2.1 Oil Palm Biomass

The success of palm oil industry in Malaysia is from the confluence of government and private sector strategies and policies. In spite of the huge production, the oil consists of only about 10% of the total biomass produced in the plantation. The remainder consists of huge amount of oil palm wastes such as oil palm trunk and oil palm fronds from the field during replanting, palm shells, mesocarp fibers and empty fruit bunch which is from the mills.

Oil palm tree normally passed their economic age, on an average after 25 years, and due to replanting, the bole length of felled palm trunk is in the range 7m to 13m, with a diameter of 45cm to 65cm, measured at breast height. About 53.87% (dry weight) of fiber bundles can be extracted from a trunk, with the remaining parts are the bark and parenchyma tissues which contribute to 14.45% and 31.68% of the dry weight of the trunk respectively.

Oil palm biomass contains quite significant amount of organic nutrient, which contributes to its fertilizer values. Basically, the oil palm biomass contains about 18 – 21% of lignin, and 65-80% of holocellulose (a-cellulose and hemicellulose), which are more or less comparable with that of other wood or lignocellulosic materials shown in TABLE 1. This makes the oil palm biomass is also suitable as a raw material for the production of pulp and paper, composites, carbon products and chemicals extraction. Oil Palm Trunk (OPT) is a bioresource because it can entirely converted into valuable chemicals and products. The most economic conversion of OPT to chemical product is production of sugars (Rahman*et al*., 2006; Kasugi*et al*., 2010). According to Chin *et al.,* 2010, controlled hydrolysis of cellulose and hemicellulose from OPT allows producing several useful chemical products such as xylose furfural, glucose and starch.

Table2.1: Proximate analysis of biomass of oil palm biomass (%, dry weight)

	Oil palm trunk	Oil palm fronds	Empty fruit bunch
lignin	18.1	18.3	21.2
Hemicellulose	25.3	33.9	24.0
a-cellulose	45.9	46.6	41.0
Holocellulose	76.3	80.5	65.5
Ash	1.1	2.5	3.5
Alcohol-benzene solubility	1.8	5.0	4.1

2.2 Natural Occurrence of Xylose

Xylose is a sugar isolated from wood and it is contains five carbon atoms and includes an aldehyde functional group and that is why it is classified as a monosaccharide of aldopentose type. A part from that, it is precursor to hemicellulose, one of the main constituents of biomass. Like most sugars, it can adopt several structures depending on conditions. With its free carbonyl group, it is a reducing sugar. According to Silva et al., xylose is the major component of the hemicellulosic fraction from vegetable biomass, is a pentose sugar that can be converted by biotechnological methods into several chemical products of high value. Same with Abd Rahman et al., 2004, approximately 24% of xylan which is a polymer made of pentose sugar xylose is recovered from the lignocellulosic waste from oil palm empty fruit bunch fiber. The conversion of xylan polymer into monomeric sugar xylose is by reduction of xylan with the presence of catalyst by hydrolyzing acid such as sulfuric acid, hydrochloric acid or hydrofluoric acid.

The natural occurrence of xylose, it is the main building block for hemicellulose, which comprises about 30% of plant matter. Xylose is otherwise pervasive, being found in the embryos of most edible plants. It was first isolated from wood by Koch in 1881. Xylose is also the first saccharide added to the serine or threonine in the proteoglycan type O-glycosylation, and, so, it is the first saccharide in biosynthetic pathways of most anionic polysaccharides such as heparan sulfate and chondroitin sulfate. Dominguez et al., 1997 ; Silva et al., 1998 ; Roberto et al., 2008 said that, the xylose recovered from lignocellulosic waste is by using the acid hydrolysis process. While, according to Kumoro et al., 2008 the lignocellulosic hydrolysis has been achieved by enzymatic hydrolysis. The most commonly method applied is acid hydrolysis and the method can be used either as a pretreatment preceding the enzymatic hydrolysis or as a method of hydrolysing lignocellulose for the sugars. As a consequence, the amount of sugars recovered from the raw material is dependent on the reaction time, temperature and acid concentration (Taherzadeh and Karimi, 2007). However, Roberto et al., 2003 mentioned that the acid concentration is the most important parameter affecting sugar yield.

Xylose is the carbon source for the growth of microorganism for the production of xylitol according to Mohamad et al., 2011. Similarly with Humairah et al., 2004, said the starting material for xylitol production is xylose. During hydrolysis process other sugars such as arabinose, galactose, glucose and some unwanted components such as acetic acid and furfural are also released. For optimum production production of xylitol it is necessary that byproducts like acetic acid and furfural concentrations in the hydrolysate are to be kept minimum for efficient bioconversion of xylose to xylitol.

Xylose is safe for use in foods. It is antibacterial and antifungal and contains natural healing agents. For this reason, it's become popular in many arenas. Xylose is a great alternative to white sugar and has none of the negative side effects of sugar. Xylose is a natural sugar that is found in some woody materials such as straw, pecan shells, cottonseed hulls, and corncobs. It is also found in berries, spinach, broccoli, and pears. It is extracted through a scientific process. In addition to this, your body actually produces a small amount of Xylose on its own.

2.3 Preparation for Samples and Extraction Method for Xylose

According to Wong *et al*. (2011), the 20-year old palm trunks were debarked chopped into chips size (20x20x20 mm^3) and grinded into powder which was sieve to obtained size of 20, 40, and 60 mesh and oven-dried at 103°C to 5% moisture content prior to futher work-up. Chemical composition of oil palm wood was determined by using TAPPI standards which are T222-74 for lignin TS os-73 for extractives, and T203 os-61 for cellulose while for hollocellulose was determined using procedure proposed by Wise and Addieco (1946). Wong *et al.* (2011), have used steeping method in order to extract the starch and sugars. They are using two steeping methods with or without 0.5% lactic acid for extracting starch. In the first method, 3.0 g of powdered palm wood which are 20, 40, and 60 mesh size were soaked with 0.2% sodium metabisulphite ($Na_2S_2O_5$) solution at room temperature

26±2°C for 24, 36, 48 or 60 h. Whereas, for the second method, powdered palm were soaked into 0.2% sodium metabisulphite ($Na_2S_2O_5$) and 0.5% of lactic acid solutions in ratio 1:5 w/w. Then, the samples were steeped at room temperature 26±2°C for 24, 36, 48 or 60 h. After that, the steeping medium was then filtered off and the residue was washed with 150mL of distilled water. At last, starch content in the filtrate was determined by VIS spectrophotometry by using iodine solution as indicator at wavelength of 650nm (Humphreys and Kelly, 1961).

Astimar*et al.* (2002) stated that, for the samples preparation, the samples was washed with water at first and dried in an oven at 50°C - 60°C until the weight is constant before grinding in a shredder and sifting into fractions of <0.3mm, 0.3 – 0.4mm, and 0.4mm. They have prepared three types of particles, the first is untreated samples which the samples were used as ground and sieve. The second is holocellulose, this was the residual comprising only hemicellulose and cellulose after the lignin was removed by bleaching using Wise and Daddieco (1946). After that, the third sample is an alkali-treated samples which were prepared from all different-siezed of samples. One portion in grams of samples was mixed with 20 portions in mL of 1% (w/v) NaOH and heated in a boiling water bath for 2hr. Then, the treated samples was then sieved out and pressed. The samples were oven dried at 50°C - 60°C until its achieved constant weight.

A part from that, similarly with Wong *et al*. (2011), Yoichi tomimura (1992) also used slightly the same technique for extracting the starch and sugars form oil palm trunk. According to Yoichi tomimura (1992), the wood samples from 25-year-old palm trunks were debarked and cut into small chips which were then crashed in order to separate vascular bundles from parenchyma. Less than 200 mesh size of